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13. ABSTRACT (Maximum 200 words)

NMR measurements were made on three classes of Nafion samples to characterize penetrant diffusion and morphology. Nafion-115 and 117 films in the acid form were swollen with dimethyl methylphosphonate (DMMP). The translational motion of the DMMP was observed using pulse field gradient NMR and the domain size of the pendant group was measured using fluorine-19 spin diffusion under conditions of high speed magic angle spinning. Both the diffusion and the domain size measurements pointed to a change in the morphology as a function of DMMP concentration with the development of larger domains at high DMMP concentration. Similar measurements of Nafion swollen with water did not involve a change in morphology. Diffusion and morphological measurements were made on calcium neutralized N-115 swollen with DMMP. Large domains and rapid DMMP diffusion were observed. Lastly cast films of Nafion-112 were prepared with and without the addition of fumed silica nanoparticles. Diffusion of water, methanol and DMMP were measure in these cast films which appeared to have smaller domain sizes and increased selectivity for water over DMMP. Also the apparent diffusion constant of DMMP was a strong function of the time over which diffusion occurred indicating a domain structure obstructing translational motion.

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(a) Manuscripts submitted but not yet published

Marcus V. Giotto, Jinghui Zhang, Paul T. Inglefield, Wen-Yang Wen and Alan A. Jones, "Nanophse Structure in Swollen Nafion by F-19 NMR Spin Diffusion Spectroscopy, submitted to ISMAR Newsletter.

(b) Papers published in peer-reviewed journals-

Marcus Giotto, Jinghui Zhang, Paul T. Inglefield, Wen-Yang Wen and Alan A. Jones "Nanophase Structure and Diffusion in Swollen Perfluorosulfonate Ionomer: An NMR Approach" Macromolecules, 2003, 36, 4397-4403.

(c) Papers published in non-peer reviewed journals or in conference proceedings-

1. P. T. Inglefield, G. Meresi, Y. Wang, A. A. Jones and W.-Y. Wen, "Permeability and Related Morphology in the Ionomer: Nafion", Polymeric Materials: Science and Engineering, American Chemical Society, 82, 172-173, (2000).
2. P. T. Inglefield, A. A. Jones, Y. Wang and W-Y. Wen "Complex Solvent Self Diffusion and Morphology in Permeable Polymers" *Polymer Preprints 42*, (**2001**) 49-50.
3. Marcus Giotto American Physical Society National Meeting, March 2002, Indianapolis "Pulse Field Gradient and Spin Diffusion NMR Study of Penetrants in Nafion Membrane", abstract number F9.010.

(d) Papers presented at meetings but not published in conference proceedings-

1. Guoxing Lin, Jinghui Zhang, Haihui Cao, Paul Inglefield, and Alan Jones, Experimental Nuclear Magnetic Resonance Conference, April 2002, Asilomar California "Simulation of Diffusion in Heterogeneous Polymers to Interpret Pulse Field Gradient Diffusion Measurements and Xenon-129 Line Shape Collapse"
2. Marcus V. Giotto, Jinghui Zhang, P. T. Inglefield, Wen-Yang Wen, and Alan A. Jones, NMR Gordon Research Conference 2003, Newport Rhode Island "Nanophase Structure and Diffusion in Swollen Perfluorsulfonate Ionomer: An NMR Approach"

(2) "Scientific Personnel" supported by this project

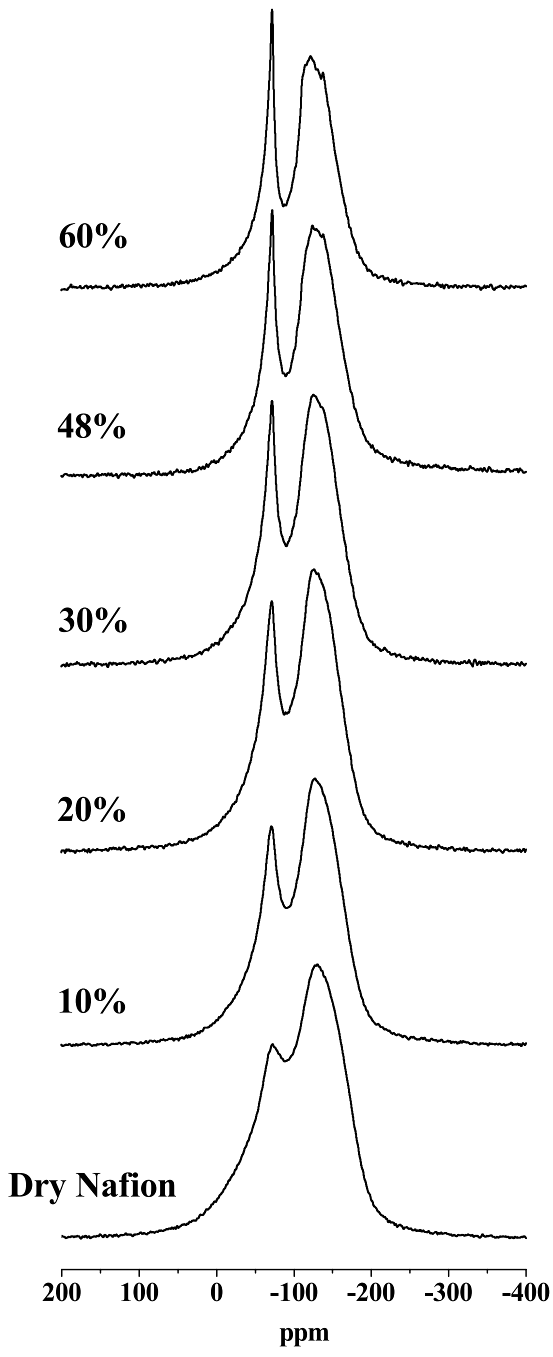
Paul T. Inglefield-principal investigator
Alan A. Jones-principal investigator
Marcus Giotto-post-doctoral fellow
Jinghui Zhang-graduate student
Nathan Schneider-consultant

(3) report of inventions-none

(4) Scientific progress and accomplishments

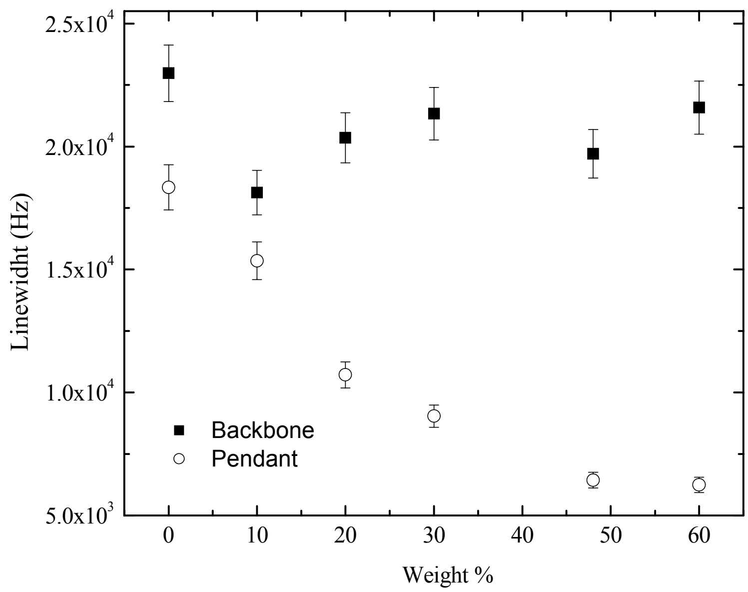
The nanophase structure of Nafion consists of perfluoroethylene domains, pendant group or side chain domains and ionic clusters. The mobility of the perfluoroethylene domains and the pendant group domains are indicated by the line widths of the static fluorine resonances associated with that part of the polymer repeat unit structure. As shown below in Figure 1, the line width associated with the pendant group (-80 ppm) decreases rapidly upon addition of DMMP indicating plasticization of the pendant group domain.

Figure 1. Static Fluorine-19 Spectra as a Function of DMMP Concentration



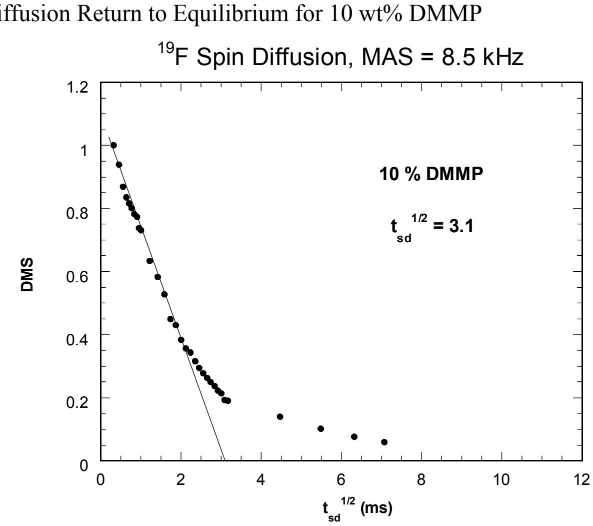
The resonance associated with tetrafluoroethylene units at –120 ppm changes little as DMMP is added indicating no plasticization of the associated domains. Fits of the spectra yield the line widths shown in Figure 2 which quantitatively demonstrate plasticization of the side group domains and not the tetrafluoroethylened domains.

Figure 2. Fluorine-19 Line Widths as a Function of DMMP Concentration



High speed magic angle spinning fluorine-19 spectra can be used to quantitatively determine the domain sizes of the dry and swollen Nafion. The morphological experiments are based on fluorine-19 spin diffusion. In Nafion there is a fortunate coincidence between the chemical structure of the polymer, the high resolution fluorine-19 NMR spectrum, and the morphology. The two major morphological domains in Nafion are the domain consisting of backbone CF_2 groups and the side chain or pendant group domain consisting of OCF_2 groups and CF_3 groups. The high resolution fluorine NMR spectrum contains two large peaks: the first resulting from the CF_2 groups and the second resulting from the OCF_2 and CF_3 groups. The second peak from the pendant group is inverted using a DANTE sequence and then the return to equilibrium is monitored. The return to equilibrium is controlled by spin diffusion from the pendant group domain to the backbone domain. A standard spin diffusion plot is used to monitor this process. A typical plot at low concentrations of DMMP is shown below.

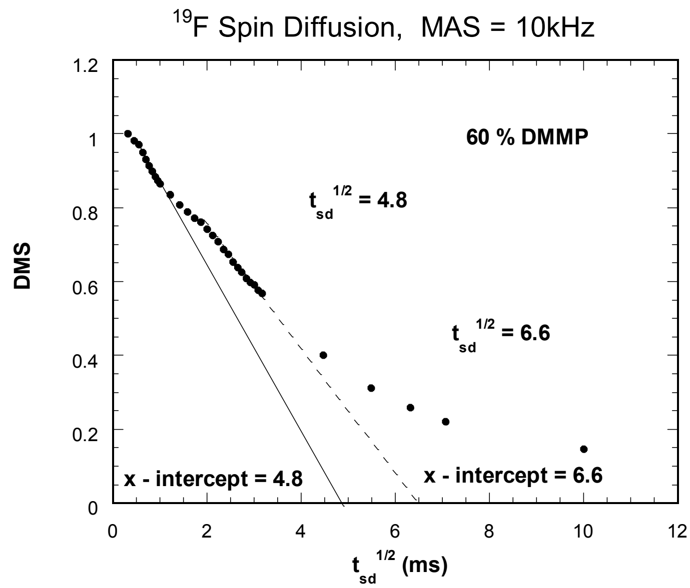
Figure 3. Fluorine-19 Spin Diffusion Return to Equilibrium for 10 wt% DMMP



The intercept on the square root of time axis is used to calculate the size of the morphological structure in terms of an overall periodicity, L, and the pendant group domain size. At low concentrations of DMMP, 0 to 20 wt %, a simple standardized spin diffusion plot is obtained and both the L and the pendant group domain size change little in this concentration range. Thus the morphology of dry Nafion is retained with a small amount of swelling of the pendant group domain noted.

At higher concentrations of DMMP, a completely different result is obtained. First the standardized spin diffusion plot has an unusual shape as shown below for 60 wt % DMMP.

Figure 4. Fluorine-19 Spin Diffusion Return to Equilibrium for 60 wt% DMMP



Instead of one time constant characterizing the return to equilibrium there appears to be two time constants. A faster time constant similar to that observed in dry Nafion and in low concentrations of DMMP is observed but now a second slower time constant is also apparent. Two intercepts on the square root of time axis can be extracted corresponding to two morphologies. The first morphology is similar in periodicity, L, and pendant group domain size to that seen at lower concentrations. The second morphology has a greater periodicity and a larger pendant group domain size. A table summarizing the morphologies observed for water and ethanol is shown first where there is only one domain size and simple swelling.

Table I. Spin Diffusion Results for Water and Ethanol in Nafion

Wt % Penetrant	$t_{sd}^{1/2}$ $(ms)^{1/2}$	f_a volume fraction	L (nm)	Pendant Domain Size(nm)
0 (Dry)	2.57	0.33	11.4	3.80
10 (H_2O)	2.73	0.453	10.1	4.59
20 (H_2O)	3.44	0.555	11.8	6.56
10 (EtOH)	4.68	0.479	16.9	8.12
17 (EtOH)	5.60	0.561	19.1	10.7
40 (EtOH)	10.8	0.752	37.7	28.4

Upon the initial addition of DMMP, fluorine-19 spin diffusion data indicates that the pendant group domain swells as it does with water. However at levels of DMMP beyond 20 wt %, the spin diffusion experiment indicated the presence of a second larger nanophase associated with DMMP and the pendant groups of Nafion. The spin diffusion data can be quantitatively analyzed to yield the fraction of pendant groups in each of the two co-existing nanophases as well as the size of the domains. The results of the analysis are summarized in Table II.

Table II. ^{19}F Spin Diffusion Results for DMMP in Nafion

Wt % DMMP	% fast	$t_{sd}^{1/2}$ fast	$t_{sd}^{1/2}$ slow	L (nm) fast	L (nm) slow
0	100	2.6	––	11	––
10	100	3.1	––	11	––
20	80	3.1	4.6	12	13
30	75	3.2	5.6	12	16
48	50	3.2	6.0	12	15
60	55	3.1	6.8	12	18

$t_{sd}^{1/2}$ = Square Root of Spin-Diffusion Time Intercept
L = Overall Structure Repeat Length

The fast decaying component in the spin diffusion experiment yields a structural repeat length of 11 or 12 nm which is similar to that seen in dry Nafion. At and above a concentration of 20 wt per cent DMMP, a second larger repeat length is observed which grows to become about half of the system when Nafion is saturated with DMMP. The structural repeat length can be broken down into the domain size for the pendant groups plus DMMP. Table III shows the results of this calculation.

Table III. Domain Size

Wt % DMMP	f_A fast	ρ^{F_A} x 10^{22} (^{19}F/cm^3) fast	f_A slow	ρ^{F_A} x 10^{21} (^{19}F/cm^3) slow	P (nm) fast	P (nm) slow
0	0.33	3.3	––		3.8	––
10	0.44	2.1	––		5.1	––
20	0.44	2.1	0.72	6.2	5.1	9.7
30	0.44	2.1	0.80	5.0	5.3	13
48	0.44	2.1	0.81	3.0	5.3	12
60	0.44	2.1	0.80	3.2	5.1	14

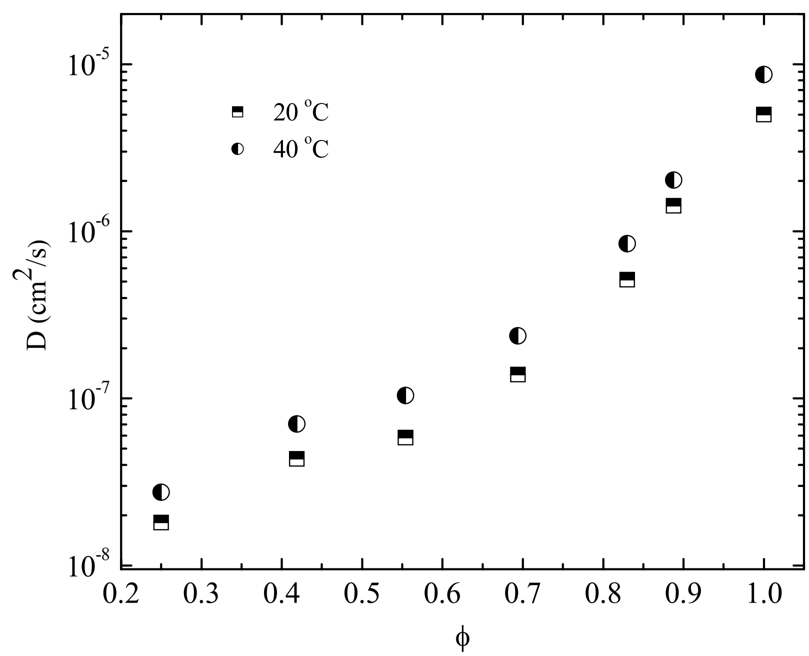
P = Pendant Domain Size

The pendant group domain sizes for the two domains are labeled P_{fast} and P_{slow}. Note that P_{slow} becomes almost three times larger than P_{fast} at the highest level of DMMP. The volume fraction of DMMP in the fast and slow domains is labeled $f_{A\ fast}$ and $f_{A\ slow}$ respectively while the density of fluorine nuclei is given by ρ_A. Thus the larger slow domain has a volume fraction of 70 to 80 % DMMP and begins to appear at around 20 wt % becoming about half of the system at 60 wt % DMMP.

What is the significance of the development of a second length scale? A large scale structural reorgainization of the morphology of dry Nafion is induced by higher concentrations of DMMP. These results are also seen in the permeability and solubility data of our collaborators (Drs. Don Rivin and Nathan Schneider) at Natick Army Research Laboratory. This change in morphology is not reversed upon removal of the DMMP according to the permeability and solubility measurements: a point that will be checked in our NMR work.

The translational mobility of DMMP was monitored by measuring the self-diffusion constant using pulse field gradient NMR. The concentration dependence (ϕ = volume fraction in the pendant group domain) of the diffusion constant is shown in Figure 5 at two temperatures.

Figure 5. Diffusion Constants for DMMP as a Function of Concentration of DMMP

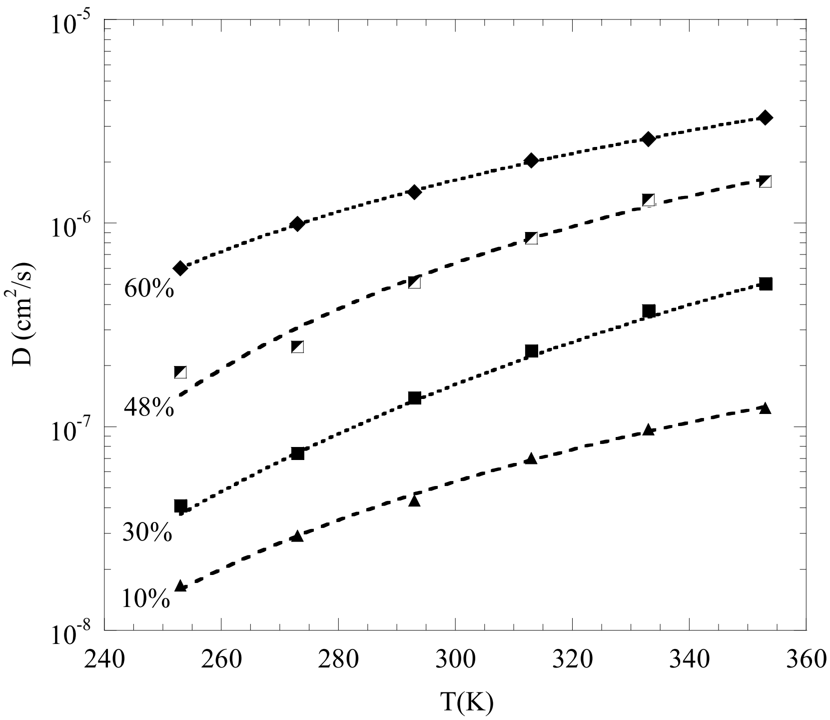


At low concentrations, ϕ less than 0.6, the plot of D versus ϕ has a downward curvature typical of the behavior seen for water in Nafion. This behavior can be described by Fujita free volume theory. However, there is a change in the nature of the data as concentration of DMMP is raised with a sharp increase in the concentration dependence of the diffusion constant. This increase is inconsistent with a change in concentration of the pendant group domain of the type which can be characterized with free volume theory. The change in behavior seen in Figure 2 occurs at the same concentration at which the new larger domain starts to appear in the spin diffusion data. The increase in the diffusion constant is ascribed to the development of the new morphology.

The structural data and the dynamical data are both consistent with a morphological transition in the system starting at a concentration of 20 wt % DMMP which is equivalent to a volume fraction of DMMP in the pendant phase of about ϕ = 0.5. This change is also seen in the sorption and permeability experiments of our collaborators, Drs Schneider and Rivin, at the Natick Labs. Their data also appears to best understood in terms of morphological change induced by the presence of DMMP. The spin diffusion experiment shows the presence of two morphologies and provides information on the associated sizes. The diffusion data also displays an unanticipated concentration dependence in that it too appears to change in form. Taken together, all the data seems to reflect a morphological transition as a function of concentration of DMMP.

The temperature dependence of the diffusion data was also investigated at a given concentration. Figure 6 contains plots of the diffusion constant as a function of temperature at several concentrations. Here the data has a smooth temperature dependence which can be described by traditional WLF equations. The actual WLF parameters associated with the lines fit to the data in Figure 6 do change in going from low to high concentrations of DMMP. Below 30 wt % , the parameters have values typical for a low molecular weight solvent in a polymer and comparable to those determined for water in Nafion. Above 30 wt %, there is an increase in both parameters to values that are rather too large for the typical solvent-polymer system. Again, the jump in the parameters is at the point where the second larger domain is becoming a significant part of the morphology. The larger WLF parameters were similar to those of ethanol in Nafion where there was also evidence for structural rearrangement and larger domains.

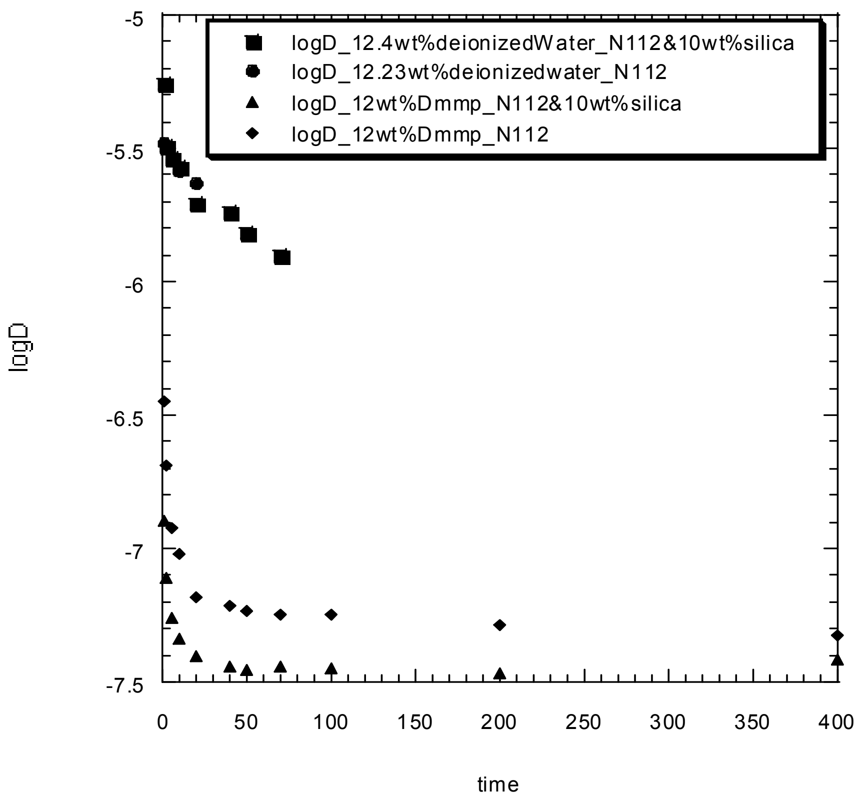
Figure 6. Temperature Dependence of DMMP Diffusion Constants at Different Temperatures



We have now acquired the same data as just discussed on the calcium neutralized form of Nafion. Here permeability data shows DMMP diffusion is slowed. The diffusion data from pulse field gradient NMR shows rapid diffusion. However, the NMR samples may have undergone a morphological transition before the measurements began. Spin diffusion measurements on the calcium neutralized Nafion indicates the same kind of morphological transition seen in the acid form of Nafion when swollen with DMMP.

The diffusion constant of water and DMMP in cast films of Nafion 112 in the acid form with and without fumed silica nanoparticles have been measure as a function of the time over which diffusion is observed. The results are shown in Figure 7. The diffusion constant of water is in the range of 10^{-6} cm^2s^{-1} and is little influenced by the addition of the fumed silica. The diffusion constant of the DMMP is about $10^{-8}cm^2s^{-1}$ and the addition of fumed silica slows diffusion by about a factor of three. The diffusion constant for DMMP is strongly dependent on the time over which diffusion is observed indicating morphological structure on the micron scale which is obstructing diffusion. Thus it appears that the nanoparticles in cast films improves the selectivity of water over DMMP which is a desirable property for applications in chemical protection. The factor of three reduction in DMMP diffusion coupled with little change in the value of water is worth further investigation.

Figure 7 Logarithm of the Diffusion Constant versus the time over which diffusion is observed. Measurements are shown for water and DMMP in cast films with and without fumed silica nanoparticles



In summary diffusion and morphology of a series of different preparations of Nafion have been examined by NMR with goal of understanding and improving the permselectivity of water over DMMP. Nafion has the desired permselctivity and it can be improved by changing the cation associated with the acid group or through the addition of fumed silica nanoparticles.

(5) Technology transfer

The results of our measurements and interpretation are shared on an on going basis with our collaborators at the Natick Army Research Laboratory. Their work guides our investigation and similarly our results helps in gaining a deeper understanding of the situation including the applicability of the materials to be used in real situations.

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